CATIONIC COPOLYMERIZATION OF BUTADIENE AND STYRENE WITH ALUMINUM CHLORIDE

BY

RUSSELL GILKEY

B.S., University of Kentucky, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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CATIONIC COPOLYMERIZATION OF BUTADIENE AND STYRENE WITH ALUMINUM CHLORIDE

Introduction

Polymerization of a diolefin leads to a polymer which may contain internal and external double bonds. Internal double bonds are formed by 1,4-addition of the monomer, while external double bonds, in the form of vinyl side groups, result from 1,2-addition. It would be desirable to synthesize a linear polymer having all internal double bonds, since such a polymer would resemble natural rubber in structure and should approach it in regard to its physical properties.

However, it has been found[1] that only 60 per cent 1,4-addition takes place when butadiene is polymerized at low temperatures with aluminum chloride as catalyst. Thus, with respect to the amount of 1,4-addition, the cationic polymer is more nearly like the synthetic copolymer GR-S than it is to natural rubber. The former has approximately 80 per cent, and the latter 100 per cent internal double bonds.

Consequently, the copolymerization of butadiene and styrene at low temperatures with aluminum chloride as catalyst was undertaken in an attempt to produce a rubber-like copolymer comparable to GR-S. The structure of the cationic copolymer has been investigated from the standpoint of a comparison with that of GR-S, particularly in connection with differences in certain physical properties and products of oxidative degradation.

Discussion Of Results

The copolymerization of butadiene and styrene at temperatures in the neighborhood of $-75°C.$, using a solution of alumium chloride in ethyl bromide as catalyst, has been investigated. It has been found that the copolymerization reaction takes place more readily as the reaction conditions

are made more anhydrous. The approach to anhydrous conditions involves the use of dry monomers and catalyst solvent, the sublimation of anhydrous aluminum chloride immediately before each run, and the conduction of the copolymerization reaction in an atmosphere of dry nitrogen. The reaction, conducted under substantially anhydrous conditions, proceeds very rapidly.

The effect of varying catalyst concentration, initial dilution, reaction time, catalyst solvent, volume of catalyst solvent and monomer ratio on the copolymerization and characteristics of the copolymer has been determined. An increase in conversion is obtained with an increase in catalyst concentration, an increase in reaction time, a decrease in initial dilution, and a decrease in volume of catalyst solvent. Increasing the ratio of styrene to butadiene causes an increased rate and degree of polymerization since styrene reacts faster than butadiene. The use of alkyl bromides other than ethyl bromide as catalyst solvent does not affect the copolymerization reaction materially except when *t*-amyl bromide is used. With *t*-amyl bromide as catalyst solvent a soluble viscous copolymer is obtained at a conversion of 100 per cent.

With ethyl bromide as catalyst solvent a hard brittle copolymer, practically insoluble in benzene, is obtained at conversions greater than 40 per cent. At conversions between 20 and 30 per cent a soluble, rubber-like copolymer is obtained. However, intrinsic viscosities for these copolymers are very low (below 0.6). A rubber comparable to GR-S could not be obtained under any set of conditions.

A comparison has been made between the cationic copolymer and GR-S in relation to molecular weight, per cent styrene, ultraviolet and infrared absorption, per cent unsaturation, and products of oxidative scission of double bonds. The soluble cationic copolymer has a much lower molecular weight than GR-S. The styrene content in the soluble copolymer is around 50 per cent. The soluble cationic copolymer is analogous to GR-S with respect to infrared absorption and

per cent unsaturation. However, a comparison of ultraviolet absorption and the products of oxidative scission indicates that there is a structural difference between the two copolymers.

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VITA

The author was born in Hopkinsville, Kentucky, on November 19, 1920. He attended the public schools of that city and was graduated from Hopkinsville High School in 1939. In the fall of that year, he entered the University of Kentucky from which, in 1943, he received the degree of Bachelor of Science in Industrial Chemistry. From April, 1943, until April, 1945, he was employed as a chemist by the B. F. Goodrich Company of Akron, Ohio. After serving in the United States Navy from May, 1945, until April, 1946, he returned to the B. F. Goodrich Company for employment during the summer. He entered the Graduate School of the University of Illinois in September, 1946. Since February, 1947, he has been employed as a Special Research Assistant on the Rubber Reserve Research Program.

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